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(54) Title: CROSS-LINKABLE AQUEOUS COATING COMPOSITIONS

(57) Abstract

An aqueous cross-linkable coating composition which contains as a binder an addition polymer dispersion containing acetoacetate function groups combined with a polyoxyalkylene polyamine amine.

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CROSSLINKABLE AQUEOUS COATING COMPOSITIONS

TECHNICAL FIELD OF THE INVENTION

This invention relates to crosslinkable binders for water-borne coatings and in particular to binders where crosslinking is provided by acetoacetate and amine functional groups.

BACKGROUND OF THE INVENTION

Polymeric coatings for use on a variety of substrates for protective and decorative purposes are well known. When in liquid form prior to application they usually have volatile organic solvents or water as the liquid carrier phase which evaporates after application to leave a solid film of a coating on the substrate. It is also well known to improve the coating performance, for example, its hardness and solvent resistance by causing them to become crosslinked or cured after application to the substrate. These harder more solvent resistant properties are advantageous when abrasive or organic solvent containing household cleaners are used. To achieve crosslinking or curing it is known to employ crosslinkable coating compositions whereby the composition includes components which react to cause crosslinking after application. Such reaction may be augmented or catalysed by the presence of atmospheric oxygen as in the case of alkyd coatings and these are widely used for decorative paints, particularly for trim paints where hard tough films are desirable. However, these coatings usually have organic solvent as the carrier phase. Alternatively the crosslinkable binder may have reactive and co-reactive groups which covalently co-react to form a crosslinked coating.

Crosslinking reactions are of course not intended to take place to an unacceptable degree until after the composition is applied to the substrate. In crosslinkable paints that rely upon external agents such as atmospheric oxygen or moisture to trigger or catalyse the crosslinking reaction, can-stable one-pack products can be prepared.

However, where the binders contain complementary reactive groups the pot life of these products is so short that the products can only be effectively used as a two-pack product where the complementary reactive groups are kept apart in separate packs until the packs are combined shortly before application to the substrate. However for many applications, particularly for DIY decorative products, this is inconvenient and it is desirable to have one-pack products.

10 With binder compositions that have complementary reactive groups attempts have been made to improve the pot life of compositions by using blocking groups that shield one of the reactive groups until the blocking group is removed after application. However, in practice, these techniques only have been useful for improving the pot life of two-pack products and also suffer from the adverse consequence of releasing the blocking agent to the atmosphere. This is undesirable, particularly for a decorative paint where the release of organic compounds to the atmosphere should be minimised.

 A potentially useful and known class of coating compositions comprises an acetoacetate functional polymer, e.g. an acrylic polymer or a polyester, and a polyamine. Such compositions are described, for example, in Journal of Coating Technology, Vol. 61 (771) pages 31-37, 1989, which involves crosslinkable polymers in organic solvents. In this article it is postulated that crosslinking occurs by means of enamine formation between the enolic acetoacetate groups and the amine groups. However, compositions with acetoacetate and amine complementary reactive groups are restricted to two-pack compositions in organic solvents.

 It has been proposed to increase the pot-life of compositions containing acetoacetate and amine groups by blocking the amine groups of the polyamine with a ketone or aldehyde to form corresponding ketimine or aldimine compounds prior to mixing with an acetoacetate-functional

- polymer. Examples of such non-aqueous compositions are disclosed in US Patent 4772680. On coating formation, exposure to adventitious moisture results in regeneration of the free amine groups which are then available to effect crosslinking. Hence, even though improved stability is claimed to be achieved by specific aromatic aldimines volatile by-products are still formed and the compositions have no application in water-borne coatings and are restricted to coatings using organic solvents as the carrier.

Aqueous or water-borne coatings are preferred from safety and environmental perspectives compared to coating compositions containing volatile organic solvents. Accordingly, water-borne coatings have been widely used for many years especially as decorative paints. One common binder for this market area comprises a film-forming aqueous dispersion of thermoplastic polymer particles which after application and evaporation of water coalesce and form a continuous film. There is usually a compromise between the ability to coalesce and form a film and the ultimate hardness of the film. Soft particles or particles with a low glass transition temperature (T_g) coalesce well but compromise properties such as block resistance and mar resistance. This compromise may be improved by the use of minor amounts of volatile coalescents or plasticisers. These agents assist particle coalescence and film formation and allow the use of harder particles having higher T_g . Ultimately the coalescent evaporates and leaves the final film with enhanced hardness and related paint properties. Whilst films with improved hardness can be prepared using this technique these films are still somewhat softer than conventional organic solvent-borne alkyds and are inadequate where hard tough films are required as for example with household trim paints. Furthermore, there is increasing environmental concern about the use of such volatile plasticisers in water-borne paints as pressure increases towards having coatings with zero volatile organic compounds (VOC).

One route to enhancing film properties of water-borne dispersion polymer coatings is to introduce a measure of crosslinking. A recent paper by Kyu-Jun Kim and Roy C Williams entitled "Utilisation of the Novel Acetoacetate Chemistry in Solvent and Water-Borne Coatings" was presented at the Water-Borne, Higher-Solids and Powder Coatings Symposium February 24-26 1993 and published in the Proceedings of the Twentieth Water-borne, Higher-Solids and Powder Coatings Symposium by the Department of Polymer Science, The University of Southern Mississippi, USA. This paper describes an anionically stabilised aqueous polyurethane dispersion containing acetoacetate functional groups which is combined with a multifunctional blocked aromatic aldimine crosslinker. One-pack coatings are described where the aromatic aldimine crosslinker is hydrophobic and of short chain length. These compositions hence suffer from the disadvantages described previously of using volatile blocking groups. The considerable efforts to obtain one-pack crosslinkable coating system are exemplified by the work described in this paper. The authors report the unacceptability of non-blocked polyamines for one-pack can stability and also the unsuitability of aliphatic ketimines in water based coatings because of their moisture sensitivity.

An alternative route to can-stable one-pack crosslinkable aqueous dispersion coating products utilising acetoacetate functional group is disclosed in Australian Patent Application Number AU-A-89709/91 in the name of Rohm and Haas Company published on 25 June 1992. In that patent application pendant acetoacetate functional groups are preferably modified to pendant enamine functionality by reaction with volatile primary amines. The binder of this publication relies upon the presence of autoxidisable groups in combination with the acetoacetate functionality. These compositions accordingly suffer from the disadvantage of the presence of volatile organic blocking agents as well as the complication of requiring the presence of autoxidisable groups to effect crosslinking.

US Patent 5,270,380 of Adamson et al discloses aqueous compositions where the dispersion polymer contains acetoacetate groups which are pre-reacted with complementary reactive groups attached to a modifying compound. The object of this invention is to increase the open time of aqueous coating compositions. To achieve this objective it is important that the reaction occurs before the composition is applied and which is clearly not intended to further react after film formation.

It is an object of the present invention to provide aqueous binders that include acetoacetate functional groups that overcome at least some of the problems with prior art binder systems.

SUMMARY OF THE INVENTION

This invention provides in one form a crosslinkable coating composition comprising an aqueous film-forming dispersion of addition polymer comprising acetoacetate functional groups and an essentially non volatile polyamine having at least two primary amine groups and wherein the mole ratio of acetoacetate to primary amine groups is between 1:4 and 40:1.

Preferably the acetoacetate groups are provided by copolymerising addition polymerisable monomers containing acetoacetate functional groups.

More preferably the acetoacetate groups are incorporated by polymerisation of a monomer selected from the group consisting of allyl acetoacetate, acetoacetoxylethyl methacrylate, acetoacetoxypentyl methacrylate and acetoacetoxylbutyl methacrylate and the corresponding acrylates.

Most preferably the acetoacetate groups are incorporated by polymerisation of acetoacetoxylethyl methacrylate (AAEM).

Preferably the polyamine is a polyoxyalkylene polyamine.

Preferably the polyoxyalkylene polyamine has the alkylene selected from ethylene and propylene or mixtures thereof.

Preferably the aqueous dispersion is sterically stabilised and more preferably it has polyoxyalkylene chains, and most preferably polyoxyethylene chains that confer steric stability.

Preferably the mole ratio of acetoacetate to primary amine groups is between 1:1.5 and 15:1, more preferably between 2:1 and 8:1 and most preferably about 4:1.

Preferably the coating composition comprises a blend of soft and hard polymer particles.

15 DETAILED DESCRIPTION OF THE INVENTION

The aqueous film forming dispersions of this invention are usually copolymers of the acetoacetate functional monomers and other addition polymerisable comonomers. Examples of useful comonomers include alkyl acrylates and methacrylates where the alkyl group has 1 to 20 (and more preferably 1 to 8) carbon atoms, styrene, vinyl acetate, butadiene, acrylonitrile and simple or substituted olefins. Monomers containing other functional groups such as hydroxyl or carboxyl groups may be used. However, we have found best results are achieved when carboxylic acid groups are kept to a minimum or absent as the presence of carboxyl groups tends to have an adverse effect on can stability. This is particularly the case when the polyamine is not a polyoxyalkylene polyamine. Preferably, we have found that the acid value of the disperse polymer should be less than 10mg KOH/g, more preferably less than 4mg KOH/g and most preferably less than 2mg KOH/g. Minor amounts of functional monomers directed towards specific objectives such as adhesion promotion may also be incorporated. The

selection of comonomers and their relative proportions is based on well established principles in the art and generally balance properties such as exterior durability, toughness and hardness with cost. The molecular weight of the copolymers is generally similar to known latexes and typically would be at least 40,000 (Mn). A light gelling structure in the particles is permitted in a similar fashion to the gel structure achieved by including minor amounts of polyfunctional acrylate or methacrylate monomers, provided that film formation is not unacceptably compromised.

The minimum film forming temperature (MFT) of the aqueous dispersion is usually in the range of 0 - 30°C which is similar to commercially available dispersions of aqueous film formers. In general, to achieve these MFT's the addition polymerisable monomers are selected so that the Tg of the copolymer is approximately similar to the desired MFT.

We have additionally found surprisingly that particularly beneficial coatings may be achieved by combining at least two dispersions having different Tg's. For example, improved early film properties such as hardness are achieved when the combination of film forming dispersions of 44% of Tg -30°C and 56% of Tg +50°C is used. Whilst acceptable results can be achieved by incorporating the acetoacetate functional groups into only one of the dispersions, the acetoacetate groups are preferred to be present in both dispersions for best results. By film forming dispersions we mean that the composition may comprise a soft and hard dispersion where the hard dispersion does not of itself form a continuous film at the temperature of use but the blend of soft and hard does form such a film, optimally aided by a minor amount of volatile coalescent.

The aqueous dispersions of the present invention may be prepared by known means such as emulsion polymerisation.

However best results are achieved where the aqueous dispersion is prepared such that it is sterically stabilised. The term sterically stabilised is an art recognised term in colloid science and means that in aqueous systems colloidal stability is conferred by the presence of a sheath of water soluble polymeric and uncharged oligomeric chains anchored to the particle surface. By sterically stabilised dispersions we mean that whilst other types of stability, such as anionic or cationic, may be present there is stability conferred by steric stabilisation. Preferably steric stability is conferred using polyethylene oxide chains. For the purposes of this invention a convenient test to ascertain whether the dispersion is sterically stabilised or not is to increase the ionic concentration of the aqueous phase to such an extent that ionic stabilisation is nullified and then to assess the stability of the dispersion. If it remains stable under these conditions we regard it as sterically stabilised. It is believed that in this invention the use of sterically stabilised particles confers enhanced can stability and reduces premature crosslinking. It is believed that, in our preferred compositions, steric stabilisation of the particles by polyoxyalkylene chains contributes to good can stability when the polyamines are polyoxyalkylene polyamines.

The compositions of the present invention are particularly suitable for gloss and semi-gloss paints. For these types of paints we have found it to be advantageous to achieve the desired gloss to use small particle size polymer dispersions, especially for the high Tg polymer dispersion where the binder consists of a mixture of low and high Tg dispersions. The particle size should preferably be less than 200 nm in diameter, more preferably less than 150 nm and most preferably less than 100 nm. Preferred paints have a gloss of at least 10 (60° head) and more preferably 40 (60° head).

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Also within the scope of the present invention are
polymer dispersions which have a core shell structure
whereby the polymer composition at the outer shell of the
particle differs from those towards the centre of the
5 particle.

Whilst a number of monomers may be used to introduce
the acetoacetate functionality, AAEM is the preferred
monomer and in practice levels from 2-30% by weight of the
disperse polymer confer useful properties. However, levels
10 of 4-20% and 5-12% give best results. This monomer is
relatively expensive and hence in practice its level is
minimised consistent with achieving the extent and rate of
crosslinking desired together with desired can stability.
In practice satisfactory can stability equates to typical
15 periods of time and temperature conditions that a product
may be on the shelf before it is applied.

Accelerated testing at elevated temperatures, such as
50°C, over shorter periods of time provides a good basis to
predict storage behaviour at ambient temperatures. In
20 practice, if after storage at 50°C for 1 week the coating
performs adequately. This is an accurate prediction of
sufficient storage stability behaviour for practical
applications.

The polyamine component is essentially non-volatile
25 and has at least two primary amine groups. By "essentially
non-volatile" we mean in normal use the polyamine component
does not become introduced into the atmosphere. Generally
this means the polyamine component has a vapour pressure
less than 0.1 mm Hg at 25°C. This is the definition
30 sometimes used by the paint industry to define compounds
necessary for zero VOC compositions. Obviously in this
invention the reactivity of the polyamine is a factor that
influences its volatility in practice enabling nominally
volatile polyamines to be used provided they react before
35 they significantly volatilise.

Preferably the polyamine contains polyoxyalkylene chains, especially ethylene and propylene.

Whilst there is a requirement of a minimum of two primary amine groups, further amine groups such as primary and secondary amine groups may be present.

Preferably the polyamine is water soluble and by this we mean it has a water solubility of at least 100g/litre though preferably it should be fully miscible with water. This is surprising in the light of the Kim and Williams paper previously discussed where they found in their aqueous dispersion system that increased hydrophilicity led to poorer can stability.

Best results are achieved when the polyamine is an ethoxylated polyamine of molecular weight 600 as supplied by Texaco under the trade name Jeffamine ED600. Other suitable polyamines are - Jeffamine ED900, D400 and EDR148.

To achieve best results the mole ratio of acetoacetate functional groups in the disperse phase to primary amine groups is approximately 4:1, and this in practice means the weight ratio between the dispersion (NV) and polyamine (NV) is approximately 100:4. As the ratio of primary amine to acetoacetate group increases can stability tends to deteriorate. Although 4:1 is the preferred ratio quite a wide range of ratios give acceptable coatings. Obviously the best ratios depend on the polyamine used as well as the aqueous polymeric dispersion, but the best ratios can be readily ascertained by a series of ladder experiments that varies the ratios systematically.

Crosslinking of the films formed by the compositions of our invention is an essential feature. In practice crosslinking can be conveniently measured by solvent resistance, such as xylene "double rubs" as known in the art.

The binders of the present invention may be combined with pigments and other conventional paint additives to produce corresponding paints with desirable properties. In some formulations volatile plasticisers are not necessary and therefore the paint may be formulated to comply with the zero VOC requirement. In other formulations minor amounts of co-solvents that function as wet edge solvents, volatile plasticisers and modifiers may be used and coating compositions that include these additives or modifiers are still regarded as aqueous coating compositions. Typically these additional volatile organic substances would not exceed 10% by weight of the total compositions as applied. Whilst significant levels of volatile organic compounds are to be avoided the coating compositions of this invention are aqueous coatings provided water is the major portion of the volatile phase.

The invention will be further described by reference to preferred embodiments in the following examples where all amounts are designated as parts by weight.

20 Example 1

A. Preparation of a coating composition where the polymeric dispersion has a Tg of 9°C, is sterically stabilised and contains 10% AAEM, the amine crosslinker is an ethoxylated polyamine and the mole ratio of acetoacetate to primary amine groups is 4 to 1.

<u>Stage</u>	<u>Material</u>	<u>Wt%</u>
A	Water	6.34
	Fatty alcohol ethoxylate *	0.24
	t-Butyl perbenzoate	0.08
	30% Hydrochloric acid	trace
B	1% Iron (II) sulphate aqueous solution	0.94

<u>Stage</u>		<u>Material</u>	<u>Wt%</u>		
5	C	t-Butyl perbenzoate			0.30
			1	2	3
	D	Methyl methacrylate	2.72	4.85	15.09
		Butyl acrylate	2.34	4.17	12.98
		Acetoacetoxyethyl methacrylate	0.56	1.00	3.12
10		Fatty alcohol ethoxylate	1.67	0.89	1.88
		Water	5.47	8.21	24.86
	E	Sodium erythorbate	0.02	0.04	0.14
		Water	0.25	0.45	1.39

* As described in Example 2 of International Patent Application PCT AU/90/00565

Stage A was charged to a reaction vessel equipped with stirrer, condenser, nitrogen blanket and feed facilities. The pH was adjusted to 3 with the hydrochloric acid, warmed to 30°C, and then B was added. D and E are combined and designated feeds 1, 2 and 3 and each was emulsified under high shear and added successively over 50 minutes, 45 minutes and 120 minutes respectively. The reaction mixture was maintained at 30°C, throughout the reaction process. After polymerisation the non-volatile content (solids) was 50.3%, particle size 95 Nm (Dn), and this dispersion was designated 1A.

B. Preparation of a semi-gloss white paint using dispersion 1A.

<u>Stage</u>		<u>Material</u>	<u>Wt%</u>
30	A	Water	4.95
		Teric 16A29* (25% in propylene glycol)	1.23
		AMP-95 (2 amino methyl propanol)	0.42
		Bevaloid 4226 (antifoam)	0.15

	<u>Stage</u>	<u>Material</u>	<u>Wt%</u>
	B	Titanium dioxide	21.16
		Calcium carbonate extender	3.36
		Clay Extender	3.36
5		Wax, S-381-N1 (Shamrock)	0.50
		(Modified polyethylene)	
	C	Dispersion 1A	55.73
	D	Texanol (coalescent)	0.89
		Bevaloid 4226 (antifoam)	0.15
10		Proxel GXL (biocide)	0.08
		Propylene glycol	2.28
		Water	3.01
		Jeffamine ED600	0.95
15		Rohm and Haas QR708 (associative thickener 50% w/w in propylene glycol)	1.78
		* alcohol ethoxylate surfactant	

20 A stage was loaded to a dispersion vessel and premixed B stage slowly added with a gradual increase in stirrer speed. High speed dispersion was effected after 15 minutes. The stirrer speed was reduced and C stage was added slowly. D stage ingredients were consecutively added with continuous steady stirring which continued for a further 20 minutes. This paint was designated paint 1B.

25 C. Test methods for Paint

Paint, pigmented or unpigmented, was tested by casting a film using a 175 micron doctor blade. Films were cast onto polypropylene panels. These films were then allowed to dry for 1 week at 25°C before being tested.

30 Meanwhile a sample of the (fresh) paint was placed in a sealed vessel and aged in an oven at 50°C for 1 week.

After 1 week ageing at 50°C a second film was cast from this wet paint. This film was also allowed to dry for 1 week (25°) before being tested.

In an alternative storage test the wet paint sample was aged at ambient temperatures (25°C) for three months. To distinguish the two tests when setting out the results the first test is designated "50°C" and the second
5 test "25°C".

The dry films were tested by rubbing with a soft cloth soaked in xylene. Rubs were performed by hand using a steady and even force. "Double rubs" (i.e. one forward and backward motion) were counted until a complete segment
10 of the film had been removed. This figure was then recorded. All testing was performed using duplicate films and the mean figure quoted.

The difference between the double rub score of the first panel and that from the aged paint indicates the
15 degree to which the paint retains its crosslinking potential. i.e. can stability.

D. Results for paint films of paint 1B.

	Fresh Wet Paint 1B	Aged (50°C) Wet Paint 1B
20 Xylene resistance of one week old film	>200	>200

These results indicate excellent crosslinking was achieved before and after storage of the wet paint.

25 Example 2

This is a comparative example which shows the importance of the presence of acetoacetate groups in the polymeric dispersion.

A paint was prepared in a similar manner to that
30 of Example 1 except that dispersion 1A was replaced with an identical dispersion save for the absence of the AAEM monomer (Dispersion 2). The particle size was 85 nm and solids 51%. Slight adjustment to the monomer ratios was

necessary to provide the same Tg of 9°C as in dispersion 1A. The paint formulation was as follows.

	<u>Stage</u>	<u>Material</u>	<u>Wt%</u>
	A	Water	4.36
5		Teric 16A29* (25% in propylene glycol)	1.18
		AMP-95 (2 amino methyl propanol)	0.40
		Bevaloid 4226 (antifoam)	0.15
		Jeffamine ED600	0.95
	B	Titanium dioxide	21.43
10		Calcium carbonate extender	2.73
		Clay Extender	2.73
	C	Dispersion 2	57.62
	D	Texanol (coalescent)	0.91
		Bevaloid 4226 (antifoam)	0.15
15		Proxel GXL (biocide)	0.08
		Propylene glycol	5.53
		Rohm and Haas QR708	
		(associative thickener 50% w/w in propylene glycol)	1.78
20	* alcohol ethoxylate surfactant		

The results for this paint are set out below

		<u>Fresh Wet Paint</u>	<u>Aged (25°C) Wet Paint</u>
25	Xylene resistance of one week old film.	5	7

This example showed no crosslinking, even when the fresh paint was tested.

Example 3

This example illustrates the use of an acetoacetate monomer other than AAEM. The preparative process of dispersion 1A was repeated except that the 10%

AAEM was replaced with 6.6% of allyl acetoacetate monomer. The particle size was 86 nm and solids were 49.6%. This substitution provided an equal molar level of acetoacetate function groups to that in Example 1. Minor adjustments to the methyl methacrylate and butyl acrylate monomers levels were necessary to provide the same theoretical Tg of 9°C as in dispersion 1A. Paint formulation from Example 2 was used.

The crosslinking results are set out below.

	Fresh Wet Paint	Aged (25°C) Wet Paint
Xylene resistance of one week old film	135	>200

These results show significant crosslinking both for the fresh and aged wet paint samples.

Example 4

This example illustrates a paint composition using a mixture of polymeric dispersions of differing Tg's.

A. Preparation of aqueous polymeric dispersion of Tg 50°C and AAEM level of 10%.

The process of dispersion 1A in Example 1 was repeated except that the D stage compositions were as follows:

		1	2	3
25	D			
	Methyl methacrylate	4.00	7.15	22.22
	Butyl acrylate	1.05	1.88	5.85
	Texanol	0.00	2.58	0.00
	Acetoacetoxyethyl methacrylate	0.56	1.00	3.12
30	Fatty alcohol ethoxylate	1.67	0.89	1.88
	Water	5.47	5.63	24.86

This dispersion had a solids content of 51.5%, had a particle size of 107 nm, and was designated dispersion 4A.

- 5 B. Preparation of aqueous polymeric dispersion of Tg -30°C and AAEM level of 10%. The process of dispersion 1A in Example 1 was repeated except that the D stage compositions were as follows.

		1	2	3
10	D Methyl methacrylate	0.99	1.77	5.50
	Butyl acrylate	3.96	7.07	21.97
	Glyceryl propoxy triacrylate	0.11	0.19	0.59
	Acetoacetoxyethyl methacrylate	0.56	1.00	3.12
15	Fatty alcohol ethoxyate	1.67	0.89	1.88
	Water	5.47	8.21	24.86

This dispersion had a solids content of 51%, particle size 80 nm, and was designated dispersion 4B.

- 20 C. An unpigmented paint was prepared by blending 56 parts of dispersions 4A and 44 parts of dispersion 4B with the amine crosslinker from Example 1 to provide an acetoacetate to primary amine ratio of 4 to 1 which is the same ratio as from Example 1.

25 D. Test Results

	Fresh Wet Paint	Aged (50°C) Wet Paint
Xylene resistance of one week old film	200	>200

- 30 This sample showed good crosslinking before and after storage. Furthermore, early film properties such as hardness were enhanced with this blend of dispersions when compared to the paint of Example 1.

Example 5

This is a comparative example which shows that no significant crosslinking is achieved in the absence of the polyamine crosslinker.

- 5 An unpigmented paint was prepared as in Example 4 except that the Jeffamine ED600 was omitted and the sole dispersion used was 1A. The results for crosslinking are set out below:

10	Fresh Wet Paint	Aged (50°C) Wet Paint
Xylene resistance of one week old film	6	10

Examples 6 and 7

- 15 These examples show that crosslinking can be achieved by the use of different ratios of acetoacetate to primary amine than used in Example 1. These tests were conducted with unpigmented paints.

- 20 Dispersion 1A (100 parts) from Example 1 was combined with Jeffamine ED600 (1.64 parts) (Example 6) and Jeffamine ED600 (6.56 parts) (Example 7) by slow addition of the amine crosslinker to each of the dispersion samples under low speed stirring. These unpigmented compositions were tested as in C from Example 1 to give the following results.

25	<u>Example No.</u>	<u>Acetoacetate/NH₂</u> <u>Mole Ratio</u>	<u>Xylene</u> <u>Resistance</u>
			Fresh Wet Paint Aged (50°C) Wet Paint
	6	4:1	196 >200
30	7	1:1	>200 >200

Both these compositions show good crosslinking before and after storage.

Examples 8, 9 and 10

These examples illustrate the use of alternative amine crosslinkers according to the invention in unpigmented paints, except for Example 9 which was a paint as in Example 1. Example 6 was repeated with the amine crosslinkers and the results are set out below. The amounts of amine crosslinker were adjusted to maintain the 4:1 acetoacetate/primary amine ratio of Example 6.

10	<u>Example No</u>	<u>Amine Crosslinker</u>	<u>Xylene Resistance</u>	
			Fresh Wet Paint	Aged (50°C) Wet Paint
	8	Jeffamine D400	133	200
	9	Jeffamine D2000	>200	124
15	10	Triethylenetetramine	>200	>200

Example 11

This example illustrates the use of a polymeric dispersion prepared using anionic surfactants as well as non-ionic surfactants.

- 20 A. A polymeric dispersion of Tg -13°C was prepared as follows:

	<u>Stage</u>	<u>Material</u>	<u>Wt%</u>
	A	Water	43.558
25		RK500 (Polyoxyethylene hexyl ether phosphate)	0.900
		Disodium orthophosphate	0.102
		Sodium hydroxide	trace.
	B	Methy methacrylate	0.785
		Butyl acrylate	1.271
30		Acetoacetoxyethyl methacrylate	0.108
	C	Ammonium persulphate	0.136
		Water	0.370
	D	Sodium 2-acrylamido-2-methyl-propane sulphonic acid	0.904
35		Water	5.941

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	<u>Stage</u>	<u>Material</u>	<u>Wt%</u>
5	E	Methyl methacrylate	15.626
		Butyl acrylate	25.257
		Acetoacetoxyethyl methacrylate	2.152
	F	Fatty alcohol ethoxylate surfactant	2.500
10	G	Water	0.113
		Sodium formaldehyde sulfoxylate	0.014
	H	Water	0.113
		t-Butyl perbenzoate	0.023
	I	Water	0.113
		Sodium formaldehyde sulfoxylate	0.014

A stage was loaded to a reaction vessel equipped with stirrer, nitrogen blanket and feed facilities. The charge was heated to 75°C. B stage was then added with stirring and the pH was adjusted (if necessary) to 9. C stage was added and at the completion of the exotherm D and E stages were both fed concurrently over four hours. F stage was added to E stage and dissolved in that part of E stage which had not been fed into the reaction vessel after 3 hours 24 minutes of the feeds. The temperature was maintained at 75°C throughout and for a further fifteen minutes at the conclusion of the feeds. Stages G, H and I were then added at 10 minute intervals.

The solids of this dispersion (11) was 49.5% and the particle size was 90 Nm.

C. A semi-gloss paint was prepared as in Example 1 with dispersion 11.

The results for this paint are as follows:

	Fresh Wet Paint	Aged (50°C) Wet Paint
Xylene resistance of one week old film	200	78

Whilst there is some deterioration of crosslinking on storage acceptable performance is still able to be achieved.

CLAIMS

1. A crosslinkable coating composition comprising an aqueous film forming dispersion of addition polymer comprising acetoacetate functional groups and an essentially non volatile polyamine having at least two primary amine groups and wherein the mole ratio of acetoacetate to primary amine groups is between 1:4 and 40:1.
2. A coating composition as defined in claim 1 wherein the polyamine is a polyoxyalkylene polyamine.
3. A coating composition as defined in claim 2 wherein the alkylene of the polyoxyalkylene polyamine is selected from the group consisting of ethylene, propylene or mixtures thereof.
4. A coating composition as defined in any one of claims 1-3 wherein the aqueous dispersion is sterically stabilised by having polyoxyethylene chains present.
5. A coating composition as defined in claim 2 wherein the mole ratio of acetoacetate to primary amine group is between 2:1 and 8:1.
6. A coating composition as defined in any one of claims 1-5 wherein the aqueous dispersion comprises a blend of aqueous dispersions, one having a low Tg and one having a high Tg.
7. A coating composition as defined in claim 3 wherein the acetoacetate function groups are provided by copolymerising 2-30% of acetoacetoxylethyl methacrylate.

8. A coating composition as defined in claim 5 wherein the mole ratio of acetoacetate to primary amine group is approximately 4:1.
9. A coating composition as defined in claim 4 that complies with zero VOC requirements.
10. A coating composition as defined in any one of claims 1-9 further comprising opacifying pigment and which has a gloss of at least 40 (60° head).
11. A coating composition as defined in any one of claims 1-10 wherein the acid value of dispersion polymer is less than 4mg KOH/g.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU 94/00599

A. CLASSIFICATION OF SUBJECT MATTERInt. Cl.⁶ C09D 133/08, 133/10, 133/12, 201/06,; C08F 246/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHEDMinimum documentation searched (classification system followed by classification symbols)
IPC C09D 3/74, 3/80, 133/08, 133/10, 133/12, 201/06Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU: IPC as aboveElectronic data base consulted during the international search (name of data base, and where practicable, search terms used)
DERWENT: IPC as above + Keywords emulsion or dispersion or suspension**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	US,A, 5270380 (ADAMSON et al) 14 December 1993 (14.12.93) Column 3 lines 21-60, column 5 lines 49-58	1-11
A	US,A, 4987177 (DEN HARTOG et al) 22 January 1991 (22.01.91) Column 2 line 46 to column 3 line 11	1-11
A	AU,B, 89709/91 (652402) (ROHM ANDHAAS COMPANY) 25 June 1992 (25.06.92) Page 12 line 16 to page 13 line 11	1-11

☒ Further documents are listed
in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents :	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier document but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family *
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search
21 December 1994 (21.12.94)

Date of mailing of the international search report

4 Jan 1995 (4.1.95)

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU 94/00599

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate of the relevant passages	Relevant to Claim No.
A	EP,A1, 516074 (WACKER-CHEMIE GmbH) 2 December 1992 (02.12.92) Page 2 lines 31 to 49	1-11

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/AU 94/00599

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
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US	5270380	AU	42019/93	BR	9304209	CA	2107827
		CZ	9301439	EP	593151	FI	933219
		HU	9302015	IL	106371	JP	6192595
		NO	932580	PL	299915		
AU89709/91	652402	BR	9105563	CA	2057202	CN	1062543
		CS	9103946	EP	492847	FI	916044
		HU	62925	IL	100447	JP	4296365
		NO	914829	PL	292901	ZA	9109645
EP	516074	CA	2069674	DE	4117487	FI	922448
		JP	5202195	US	5278225		
END OF ANNEX							